

EFFECT OF ALUMINUM CONTENT ON THE ACIDITY AND CATALYTIC PROPERTIES OF DEALUMINATED ZEOLITES

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The properties of dealuminated with EDTA faujasite type zeolites and synthetic samples with identical Si/Al ratios have been compared. It is concluded that the properties of faujasite structure zeolites depend not only on the Si/Al molar ratio but also on the absolute number of aluminum atoms in the unit cell.

Studying dealuminated by EDTA zeolite samples obtained from one initial sample BEAUMONT and BARTHOMEUF [1—3] have suggested that the nature of the acidity change depends solely on the number of aluminum atoms in the unit cell. By devising a mathematical model of dealumination MIKOVSKI and MARSHAL [4] reaffirmed the suggestion that the rising degree of dealumination brings about a parallel rise of strong acid sites. Moreover, the extraction of each aluminum atom causes a qualitative change in the acidity of the residual ones.

The present investigation is a further attempt to develop the ideas considering the role of the absolute number of aluminum atoms in the unite cell on the acidic

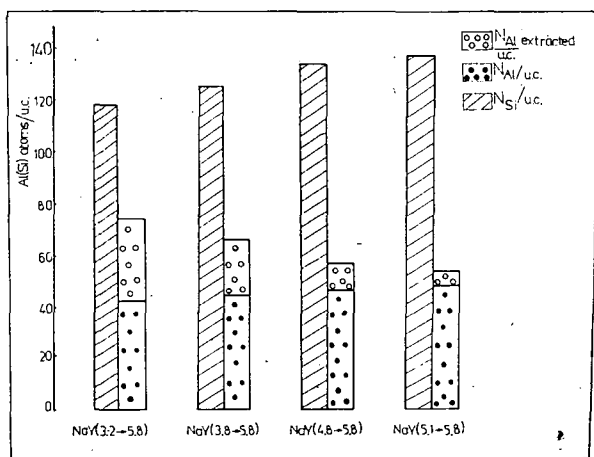


Fig. 1. Histograms for the preparation of dealuminated samples with equal Si/Al ratio from different initial samples

and catalytic properties of zeolites. The faujasite samples of various Si/Al molar ratios modified by dealumination represent a convenient basis for such a study, because it makes possible a directed and controlled variation of the contents of the two constituent unit cell's elements *i.e.* Al and Si and their ratio.

For one series of initial samples with a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.2, 3.8, 4.8 and 5.1 and an increasing Si content, to obtain samples with the same new Si/Al ratio (*e.g.* 5.8) through dealumination different quantity of Al must be extracted. Considering the fact that the Si content in the unit cell remains unchanged under the employed conditions of treatment with EDTA [5, 6], to preserve an equal ratio between the two elements in the new dealuminated series, the absolute number of Al atoms/u. c. must be different — least in the sample obtained from the initial one with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.2 and greatest in the $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$ one. Similarly, the number of Al atoms will be different in every two samples of the same Si/Al ratio, the one obtained through direct synthesis, the other — through dealumination of a sample with lower Si content.

These theoretical considerations have been confirmed by data from chemical analyses of the series of dealuminated samples obtained in the present study. It is clear that in all cases the number of Al atoms/u. c. in the dealuminated samples is lower than that of the synthetic ones having the same Si/Al ratio.

Table I

Indexes of the samples	Molar Si/Al ratio		Unit cell composition
	before dealum.	after dealum.	
HNaX(2.6)	2.6	—	$\text{H}_{35.6}\text{Na}_{47.6}(\text{AlO}_2)_{83.5}(\text{SiO}_2)_{108.5}$
HNaX(2.6 → 3.2)	2.6	3.2	$\text{H}_{22.2}\text{Na}_{46.3}(\text{AlO}_2)_{68.5}(\text{SiO}_2)_{108.5}$
HNaY(3.2)	3.2	—	$\text{H}_{33.4}\text{Na}_{40.4}(\text{AlO}_2)_{73.8}(\text{SiO}_2)_{118.8}$
HNaY(3.2 → 3.9)	3.2	3.9	$\text{H}_{39.0}\text{Na}_{21.3}(\text{AlO}_2)_{60.3}(\text{SiO}_2)_{118.8}$
HNaY(3.8)	3.8	—	$\text{H}_{42.8}\text{Na}_{23.4}(\text{AlO}_2)_{66.2}(\text{SiO}_2)_{125.8}$
HNaY(3.8 → 4.8)	3.8	4.8	$\text{H}_{26.0}\text{Na}_{26.6}(\text{AlO}_2)_{52.6}(\text{SiO}_2)_{125.8}$
HNaY(4.8)	4.8	—	$\text{H}_{34.6}\text{Na}_{21.4}(\text{AlO}_2)_{56.0}(\text{SiO}_2)_{136.0}$
HNaY(4.8 → 6.2)	4.8	6.2	$\text{H}_{32.6}\text{Na}_{10.9}(\text{AlO}_2)_{43.5}(\text{SiO}_2)_{136.0}$
HNaY(4.8 → 7.8)	4.8	7.8	$\text{H}_{33.0}\text{Na}_{11.9}(\text{AlO}_2)_{34.9}(\text{SiO}_2)_{136.0}$
HNaY(3.2 → 5.8)	3.2	5.8	$\text{H}_{31.0}\text{Na}_{9.7}(\text{AlO}_2)_{40.7}(\text{SiO}_2)_{118.2}$
HNaY(5.1 → 5.9)	5.1	5.9	$\text{H}_{38.0}\text{Na}_{8.4}(\text{AlO}_2)_{46.4}(\text{SiO}_2)_{138.0}$
HNaY'(5.8 → 8.8)*	5.8	8.8	$\text{H}_{17.4}\text{Na}_{9.6}(\text{AlO}_2)_{27.0}(\text{SiO}_2)_{118.2}$
HNaY'(5.9 → 8.9)	5.9	8.9	$\text{H}_{18.9}\text{Na}_{11.7}(\text{AlO}_2)_{30.6}(\text{SiO}_2)_{138.0}$

* Samples designated with „'” have been obtained by second dealumination.

The samples obtained by this method have proved particularly appropriate for studying the individual role of Al, by way of comparing the properties of samples with identical Si/Al ratio but with different Al content.

The variation of the acidic function and catalytic activity, depending on the Al content in samples with identical Si/Al ratio, has been followed. The method of high temperature adsorption and thermodesorption of NH_3 [11] and toluene disproportionation [12] as a model reaction has been employed.

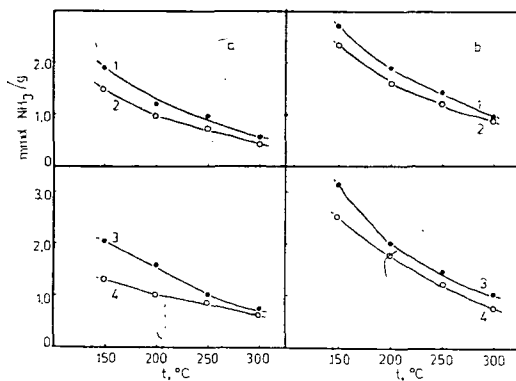


Fig. 2. Relationships between the quantity of ammonia chemisorbed and the temperature of adsorption for dealuminated and synthetic samples with the same Si/Al ratio (a): 1-HNaY (3.2→3.9), 2-HNaY (3.8), 3-HNaY (3.8→4.8), 4-HNaY (4.8), and dealuminated ones, prepared from synthetic samples with various initial Si/Al ratios (b): 1-HNaY (3.2→5.8), 2-HNaY (5.1→5.9), 3-HNaY' (5.8→8.8) and 4-HNaY' (5.9→8.9)

The data obtained from the chemisorption of NH_3 indicate that dealuminated samples adsorb larger quantities of ammonia than the initial samples despite their identical Si/Al ratios. The same regularity has been observed in dealuminated samples with practically identical Si/Al ratio obtained from different initial samples. Consequently in both cases higher acidity is observed in samples with a lower number of Al atoms/u. c. regardless that the ratio of the two elements, *viz.* Al and Si may be the same.

These result should be associated not only with the difference in the absolute number of Al atoms in the comparable samples but also with their positions in the lattice. In all probability, during dealumination a selective extraction of a part of the Al atoms takes place at definite places and order in the structure. This will affect the modification of their acidic properties.

The thus observed acidity relationships of the samples affects their catalytic properties in the same manner (Fig. 3). As it can be seen from this figure, a good correlation exists between the number of Al atoms after dealumination, the quantity of NH_3 adsorbed at 200° C and the catalytic activity. Similarly to the cracking reaction of *isooctan*

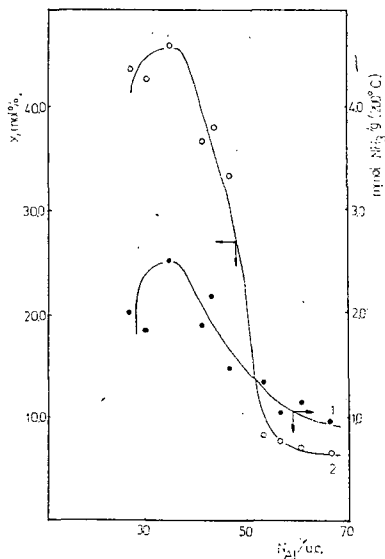


Fig. 3. Acidity (adsorption of ammonia at 200° C) and catalytic activity as a function of the Al content

[1] and cumene [10], and toluene disproportionation on bi-functional catalysts, containing Ca cations [7], maximum activity is observed in the samples containing about 35 Al atoms/u. c.

It should be emphasized, however, that the acidity differences of samples with identical Si/Al ratios, but different absolute number of Al atoms in the unit cell are much more distinct than those arising in their catalytic activity. Because of this, probably, previous studies [8, 9] based only on catalytic data do not provide information on differences from samples with the same Si/Al ratio. Besides, both acidic and catalytic differences are more pronounced when the difference of the aluminum content is higher in the comparable pairs with identical ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ (e.g. in the samples HNaY (3.2→5.8) and HNaY (5.1→5.9). This can be clearly seen from Fig. 3.

On the basis of these results the conclusion can be made that the properties of the zeolites with faujasite structure depend not only on the Si/Al ratio but also on the individual number of Al atoms in the unit cell. In all probability dealumination results in a selective extraction of Al at definite positions which causes new redistribution of the remaining atoms in the lattice. It influences their electrostatic interactions and is one of the major factors of zeolite acidity function and catalytic properties.

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